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(57) Abstract

There is provided a process for the production of a product comprising nanocrystalline particles, which particles comprise at least one metal, or at least one metal oxide, substantially dispersed on the surface of at least one metal oxide, or mixed metal oxide, which process includes the steps of (a) heating a mixture including at least one wet hydrous metal oxide, or wet hydrous mixed metal oxide, and at least one reducible metal salt to form a wet gel; (b) heating the wet gel to the decomposition temperature of the reducible metal salt; and (c) reducing the resultant composition.

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PREPARATION OF NANOCRYSTALLINE AND DISPERSIBLE SUPPORTED METAL CATALYSTS

Field of the Invention

The present invention relates to the field of the preparation of supported metal and metal oxide products, particularly catalysts.

Background

For many years, it has been known that suitably-doped ceria and zirconia solid solutions are exceptional oxygen ion conductors.

This is because the lower or higher valent dopant, for example Ln^{3+}, Y^{3+} or Zr^{4+} (wherein Ln represents a lanthanide metal), creates oxygen ion vacancies in the fluorite lattice, thus allowing facile oxygen ion transport within the lattice to the surface.

The resultant ability of these compounds to take up and release oxygen in response to the atmospheric partial pressure of oxygen, has been put to use extensively in catalysis. Here, an "active" (i.e. catalytic) metal (or metal oxide) on the surface of an oxygen ion conductor catalyses redox reactions with atmospheric gases. An example of this is in exhaust emission control (catalytic converters), where oxygen may react with CO gas, or unburned hydrocarbons, to form CO_2 and water (oxidation), and where NO may react with CO to produce N_2 and CO_2 (reduction/oxidation).

The ability of the oxide ion conductor (the "promoting" oxide ion conductor) supporting the active metal/metal oxide in such a system to release oxygen under reducing conditions (acceleration), and to take up oxygen under oxidizing conditions (deceleration), has a direct effect upon the size of the window of oxygen partial pressures over which the active metal (e.g. Pt, Rh or Pd) is effective.

Recently, it has been shown (see, for example, *J. Catal.*, (1997) **169**, 490, *Catalysis Letts.*, (1998) **50**, 193, *Applied Catalysis B - Environmental* (1998) **16**, 105 and *J. Catal.*, **175**, 269) that ceria-zirconia solid solutions of the formula $Ce_{1-x}Zr_xO_{2-x/2}$, in the ceria rich region (i.e. those in which x = 0.15 to 0.50), are the most effective presently known redox promoters when operating at low temperatures (engine cold start). When an appropriate active metal is dispersed on their surface, these ceria-zirconia compounds have been found to greatly reduce emissions of CO, NO_x and hydrocarbons.

It follows that catalytic efficiency relies on the high dispersion of active metal on the promoter alone.

Currently available techniques for coating active metals onto metal oxide supports, namely washcoating and dispersion techniques, involve dispersing promoter oxide powders (>1 μm particle size) within high surface area supports e.g. γ-Al_2O_3, and then dispersing the active metal onto this combined washcoat. This results in the problem that a large proportion of the expensive active metal particles are dispersed on the alumina support (see Figure 1), thereby reducing the efficiency of the catalyst (in that a greater proportion is "unpromoted"), and the lifetime of

the catalytic system (a metal catalyst may sinter more readily on a support such as alumina).

In international patent application PCT/GB98/01355 (WO 98/51617), techniques for the production of metal oxide gel products as nanocrystalline aqueous dispersions (particle sizes, for example, in the range 5 to 50 nm), using cheap inorganic starting materials, are disclosed.

We have now found that this technique may be modified by including at least one reducible salt of an active metal in the initial reaction mixture in order to produce an aqueous dispersion of individual crystalline nanoparticles containing both the active metal/metal oxide and the promoter as a single phase. We have also found, surprisingly, that simple reduction of these nanocrystals results in the active metal/metal particles being substantially dispersed on the surface of the promoter oxide. This results in a process that may be employed in the preparation of *inter alia* improved catalyst products.

Disclosure of the Invention

According to the invention, there is provided a process for the production of a product comprising nanocrystalline particles, which particles comprise at least one metal, or at least one metal oxide, substantially dispersed on the surface of at least one metal oxide, or mixed metal oxide, which process includes the steps of:

(a) heating a mixture including at least one wet hydrous metal oxide, or wet hydrous mixed metal oxide, and at least one reducible metal salt, to form a wet gel;

(b) heating the wet gel to the decomposition temperature of the

reducible metal salt; and

(c) reducing the resultant composition,

which process is referred to hereinafter as "the process of the invention".

In the process of the invention, process steps (a), (b) and (c) are preferably carried out in the above order.

Although the process of the invention may be used to prepare particles that are substantially nanocrystalline in nature (i.e. up to 100% of the individual, unagglomerated crystallites have a particle size of less than 500 nm (e.g. less than 250 nm, preferably less than 50 nm)), as used herein, the term "nanocrystalline" particles, includes that no more than 1% of particles produced *via* the process of the invention are non-crystalline, and/or that no more than 1% of particles produced *via* the process of the invention exceed a particle size of 500 nm, and in which the average crystallite sizes (Z_{av}) are in the range 3 to 250 nm (e.g. 4 to 100 nm and preferably 10 to 30 nm).

By "substantially" dispersed, we include that at least 40%, preferably at least 60%, and more preferably at least 80%, of the relevant metal or metal oxide (as appropriate) is presented, e.g. as particles, on the surface of the metal oxide support, as opposed to within the matrix thereof.

The term "wet" hydrous metal oxides, and mixed metal oxides, includes systems comprising a hydrous metal oxide and water, wherein the combined lattice water and/or free water content, is present in excess of 10% w/w, and preferably between 10 and 200% w/w, of the metal oxide system, whether coordinated to the metal ions of the metal oxide system or otherwise.

The term "wet gel" as used herein includes a gel system containing a metal oxide, lattice water and, optionally, depending upon the oxide system that is employed, excess free water, wherein any excess free water that is present, is present in an excess of between 0 and 95%, preferably 0 and 70%, and especially 0 and 60%, w/w of the total weight of the gel.

We have found that step (b) of the process of the invention results in the production of deaggregated material. Thus, the heating step (b) may preferably be carried out until the reducible metal salt is decomposed and/or the product is deaggregated.

The product of step (b) may preferably be dispersed onto a suitable substrate (e.g. a high surface area support) before or after carrying out the reduction step (c). This dispersion may be achieved by dispersing the product of step (b) into a suitable medium (e.g. an aqueous solvent, such as distilled water), casting the resultant mixture onto the relevant substrate and drying as necessary.

Any non-dispersible product which may be formed following step (b) may be removed using conventional techniques. By "non-dispersible product" we include product, which is of a particle size which is too great to allow it to enter the colloidal state. For example, non-dispersible product may be removed by dispersing the product of step (b) as described above to form a sol. In such an instance, dispersion may take place with stirring over an appropriate period (e.g. approximately 1 hour) followed by standing over 2 hours. Any non-dispersible sediment may then be removed by an appropriate means (e.g. decanting the supernatant). The resultant sol, which may or may not be dialysed using techniques known

to those skilled in the art in order to remove any excess anions, may comprise a single phase nanocrystalline solid solution (i.e. it does not comprise particles of a size of greater than 500 nm, preferably greater than 250 nm, once the non-dispersible product is removed).

The nanocrystals may then be dispersed onto an appropriate substrate (e.g. γ-Al_2O_3) before carrying out the reduction step (c).

Alternatively, the reduction step (c) may be performed directly after step (b), and any non-dispersible product may then be removed by dispersing the product of step (c) into a solvent to form a sol in the above-described manner. Again, the resultant nanocrystals comprising reduced metal, or metal oxide, may then be dispersed onto an appropriate substrate (e.g. γ-Al_2O_3).

We have found, surprisingly, that reduction step (c) results in reduced metal migrating to, and being presented on, the surface of the metal oxide particles. Such metals may or may not re-oxidise (or partially re-oxidise), if subjected to an oxygen-containing atmosphere (such as air), once they have migrated to the surface such that a metal oxide (and/or mixed metal/metal oxide) is presented on the surface of the metal oxide particles (though this surface re-oxidation may be prevented if the product of step (c) is kept in a reducing environment). In this respect, the process of the invention finds particular utility in the production of products (e.g. catalysts) in which an active metal, or active metal oxide, is supported on (i.e. dispersed, or presented, on the surface of) a metal oxide (e.g. a promoter or stabilising oxide, or a solid solution of metal oxides).

Thus, the process of the invention may be used to form products

comprising a wide variety of metals or metal oxides, which are supported on metal oxide systems, mixed metal oxide systems, and/or metal oxide hydrate systems. In particular, any "active" metal (e.g. transition metal) or "active" metal (e.g. transition metal) oxide that is capable of catalysing a chemical reaction to a experimentally determinable degree may be employed in the process of the invention. Suitable active metals, include palladium, platinum, rhodium, copper, iron, chromium, silver, cobalt, ruthenium and nickel and suitable active metal oxides include those of copper.

Suitable supporting metal oxide systems include any single or multicomponent oxide system, especially those that are capable of promoting the reaction of a given active metal, and/or metal oxide, for a specific catalytic reaction. Suitable supporting metal oxides thus include lanthanide oxide systems (including, but not limited to, those of lanthanum, cerium, gadolinium, neodymium and praeseodymium), transition metal oxides (including, but not limited to, those of yttrium, zirconium, iron, palladium, nickel, titanium and chromium) and even oxides of main group metals (including, but not limited to, magnesium and aluminium). Moreover, the process according to the invention may be used to prepare mixed oxides and solid solutions of two or more of the abovementioned metals. Particularly preferred metal oxide systems include those which are promoters (e.g. promotors of redox rections), for example those of cerium, zirconium, yttrium and mixtures of such oxide systems.

We have found that the process of the invention may be used to prepare, at low temperatures, supported metal/metal oxide systems in which the supporting metal oxide system possesses a high degree of accuracy in the

desired compositional stoichiometry and a minimal point defect concentration.

Thus, according to a further aspect of the invention, there is provided a product obtainable by the process of the invention.

In the process of invention, the wet gel comprising the hydrous metal oxide may be formed (step (a)) by heating a mixture of wet hydrous oxide system and reducible metal salt, in the desired proportions. It is preferred that the heating is performed under atmospheric pressure (i.e. in an open atmosphere, rather than in a sealed vessel).

In the formation of the wet gel, the mixture may be heated such that it is dried up to a specific, or critical, oxide:free water ratio, which ratio depends upon the hydrous metal oxide(s) that is/are employed. Although the critical (minimum) amount of water that must be present in the wet gel depends upon the oxide system that is used, it can be determined non-inventively by the skilled person as the minimum amount of free water that must be present in the resultant gel that will enable deaggregation during the course of carrying out the next step in the process of the invention (step (b)). For example, the mixture may be heated until it is sufficiently dried such that it forms a gel which, depending upon the metal oxide system that is employed in the first instance, may include drying until the gel so formed is of a soft and/or crumbly consistency or drying to a constant weight (i.e. no free water). For example, systems comprising cerium oxide and aluminium oxide may be dried to a constant weight (though this is not critical). Systems comprising other oxides (e.g. those of zirconium and titanium) may be dried to form a gel with a soft and/or crumbly consistency (which may comprise e.g. 60 to 70% water (lattice

and combined) based on the total weight of the gel). The temperature at, and length of time over, which the mixture should be heated will depend upon factors such as the composition of the mixture and the degree of hydration (i.e. "wetness") of the hydrous metal oxide. However, suitable temperatures are in the range room temperature to 120°C, preferably 40 to 110°C and more preferably 55 to 110°C (e.g. 105°C), and suitable time periods are in the range 1 to 24, preferably 1 to 6, more preferably 1.5 to 5 and especially 1.75 to 4.5 hours.

The skilled person will appreciate that reducible metal salts that may be employed in the process of the invention include any salt of a metal in which the oxidation state of that metal may be lowered using conventional reducing techniques. Thus, suitable salts include metal nitrates, metal chlorides, metal perchlorates, metal acetates, metal carbonates and higher metal oxides.

We prefer that the reducible metal salt is a metal nitrate or a metal chloride.

Appropriate wet hydrous metal oxides and reducible metal salts are commercially available, are well known in the literature or are readily available using techniques which are well known to those skilled in the art, such as those described hereinafter.

Appropriate vessels which may be used to heat the mixture to form the wet gel (step (a)) will be well known to those skilled in the art and include standard evaporating dishes made from an appropriate material (e.g. pyrex).

The product of step (a) may be heated (step (b)) in a suitable atmosphere e.g. a furnace or a controlled pressure/water atmosphere by, for example, sealing in an appropriate reaction vessel (e.g. a pressure reactor vessel (e.g. an autoclave) or a hydrothermal reactor). The skilled person will appreciate that the reaction vessel may be composed of appropriate materials, which may depend upon the constituents of the wet gel.

The wet gel may, for example, be heated to the decomposition temperature of the salt. This is typically in the region of 220 to 330°C, for example 305 to 320°C, for metal nitrates and metal chlorides. Suitable heating rates are in the region 10 to 500°C per hour, for example 200°C per hour. The wet gel may be heated for between 1 and 60 minutes, preferably 10 to 30 minutes at the appropriate temperature, depending on the hydrous metal oxide system that is used and the total mass. The decomposition of the reducible salt as appropriate may be monitored *via* an appropriate means (e.g., in the case of an autoclave, by observing the presence of an endotherm by means of a temperature gauge, and/or an increase in pressure on a pressure gauge).

The heating step (b) may also be carried out in a furnace (e.g. a muffle furnace), or in an open atmosphere. Suitable heating rates are in the region 10 to 500°C per hour, for example 200°C per hour, and a heating time of between 1 and 180 minutes, preferably 30 to 120 minutes, depending on the hydrous metal oxide system that is used and the total mass.

Once step (b) has been carried out the reducible metal salt is decomposed and is substantially in the form of a reducible metal oxide that is present

within the supporting metal oxide matrix. Further, the product of step (b) is preferably deaggregated, and in the form of nanocrystals.

The reduction step (c) may be performed using standard reduction techniques, which are known to those skilled in the art, for example reduction in a suitable reducing atmosphere (e.g. H_2 in N_2; such as 5% H_2/N_2) at an appropriate pressure (e.g. atmospheric pressure) and temperature (e.g. 800°C to 1000°C).

Products obtainable by the process of the invention may be dispersed into an appropriate solvent to form a sol, which may then be used to coat or impregnate a variety of substrates in order to yield a coating which is nanocrystalline in nature. For example, products may be dispersed onto a catalyst support to form a catalyst. Other layered materials comprising coated substrates may be readily produced in a similar fashion. It will be appreciated by the skilled person that the process of the invention offers the flexibility that the reduction step (c) may be performed before or after dispersion on a substrate.

Products obtainable by the process of the invention have the advantage that, following the reduction step (c), metals/metal oxides may be dispersed substantially to entirely on the surface of a metal oxide system (e.g. a promoter or stabilising oxide). Thus, when the product to be prepared is a catalyst system, the process of the invention has advantages over standard active metal/metal oxide deposition techniques described hereinbefore, which prior art techniques result in a lower proportion of active metal/metal oxide being dispersed on the promoting oxide system (see Figure 1). Conversely, the process of the invention may result in catalyst products in which less than 1% (e.g. none) of the metal/metal

oxide is presented on the catalyst support, and thus catalyst products possessing a higher surface area of active metal/metal oxide. This may greatly increase the catalyst efficiency and lifetime of the resultant catalyst.

The process of the invention also has the advantage that a wide variety of cheap, readily available inorganic precursors may be used.

Examples

The invention is illustrated, but in no way limited, by way of the following examples, in which:

Figure 1 illustrates the structural differences between a catalyst produced using the process of the invention, and according to the prior art.

Figure 2 shows an x-ray diffraction pattern for (a) $Ce_{0.75}Zr_{0.2}Pt_{0.05}O_{2-\delta}$ sol dried at 100°C, and (b) the same gel following reduction at 850°C for 3 hours in 5% H_2/N_2.

Figure 3 shows an x-ray diffraction pattern for (a) $Ce_{0.8}La_{0.15}Cu_{0.05}O_{2-\delta}$ sol dried at 100°C, and (b) the same gel following reduction at 850°C for 3 hours in 5% H_2/N_2.

Figure 4 shows an x-ray diffraction pattern for (a) $Zr_{0.78}Y_{0.2}Rh_{0.02}O_{2-\delta}$ sol dried at 100°C, and (b) the same gel following reduction at 850°C for 3 hours in 5% H_2/N_2.

Characterisation

Morphology and elemental analysis

This was carried out on dried gel or calcine samples using out a JEOL scanning electron microscope operating at 20 kV and equipped with an energy dispersive x-ray analyzer. Conducting samples were prepared by either carbon coating or gold sputtering finely ground powder specimens. Both broad beam and point EDX analysis of powder particles were performed using pure manganese as a reference standard.

X-ray powder diffraction patterns of the samples were recorded in the region of $2\Theta = 10\text{-}80°$ with a scanning speed of 1/4°/min on a Philips diffractometer using CuK_α radiation with a nickel filter. The average crystallite size of each composition was calculated from the broadening of a specific diffraction peak using the well-known Scherrer equation, $D = k\lambda/h_{1/2}\cos\Theta$, where D = average size of the crystallites, k = Scherrer constant, λ = wavelength of radiation, $h_{1/2}$ = peak width at half height and Θ corresponds to the peak position.

Particle Size

This was measured in solution by photon correlation spectroscopy or on solid samples by transition electron microscopy.

Example 1

Platinum Catalyst on a Ceria/Zirconia Solid Solution

(i) Ceria Hydrate

$Ce(NO_3)_3.6H_2O$ (50 g) was added to 250 mL of distilled water and dissolved at room temperature. Separately, conc. ammonia solution (880

s.g.; 30 g) and hydrogen peroxide solution (27.5% wt.; 17.5 g) were dissolved in 150 mL of distilled water and were added rapidly to the cerium solution with stirring. Stirring was continued for 5 minutes to give a deep red/orange precipitate. The mixture was diluted to 750 mL with distilled water and centrifuged at 2000 rpm for 5 minutes, removing the supernatant. The resultant solid was washed with 4 x 750 mL of distilled water, with centrifuging in between to remove all anions and excess precipitating reagents. Finally, the precipitate was slurried to a 250 mL total volume, and 2M HNO_3 was added dropwise with stirring until a pH value of 6 was attained. Heating of the resultant mixture to 50°C with stirring resulted in a banana yellow precipitate. Centrifuging at 3000 rpm for 5 minutes, and removal of the supernatant, yielded a crystalline ceria hydrate with a primary crystallite size of 20 Å.

(ii) Platinum Catalyst on a Ceria/Zirconia Solid Solution

A zirconium oxynitrate solution was prepared made by adding $ZrO(CO_3)_2.xH_2O$ powder (7.67 g) to 15 mL of distilled water and mixing to a thin slurry. Conc. HNO_3 acid (5 g) was then added and the resultant mixed until the fizzing stopped. The mixture was then heated briefly to give a clear solution. Separately, $H_2PtCl_6.xH_2O$ (3.2 g) was added to 10 mL of distilled water containing 2 drops of conc. HNO_3 acid and dissolved. The platinum salt solution was then added dropwise with stirring to the zirconia solution to give a deep red/orange solution. This was then added to 25 g of ceria hydrate (75.4% CeO_2; from step (i) above), mixed thoroughly and dried to constant weight at 60°C. The mixture was then lightly crushed and added to a pyrex beaker to a 1.5 cm bed depth. This was then heated in a muffle furnace to 260°C for 2 minutes at a heating rate of 200°C/hr, removed from the furnace and cooled. The resultant orange powder was finely ground and added with

stirring to 850 mL of distilled water and stirred for 30 minutes. The resultant sol was then centrifuged for 10 minutes at 4000rpm to remove any non-dispersible product (<5%). The sol was orange, transparent and stable, and consisted of single phase crystalline fluorite structured nano-particles (see Figure 2(a)) with an average particle size of about 10 nm and a primary crystallite size of about 5 nm. This sol was used to impregnate a suitable high surface area and porous support (γ-Al_2O_3), dried and fired to 600°C for 30 minutes. The catalyst was then activated by reduction at 850°C for 2 hours in 5% H_2/N_2, producing platinum metal finely dispersed on the surface of $Ce_{0.8}Zr_{0.2}O_{2-x/2}$ nanocrystals, which in turn were dispersed on γ-Al_2O_3. (See Figure 2(b), which shows the X-Ray diffraction pattern of the reduced undispersed nanocrystals.)

Example 2

A Highly Dispersed Cuprous Oxide Catalyst

$La(NO_3)_3.5H_2O$ (8.47 g) was added to 15 mL of water and dissolved. To this, $Cu(NO_3)_2.3H_2O$ (1.645 g) was added and dissolved. The solution was added to 25 g of ceria hydrate (75.4% CeO_2; see Example 1(i) above) mixed thoroughly and dried to constant weight at 60°C. The dried mixture was lightly crushed and placed in a pyrex beaker to a bed depth of 1.5 cm. The mixture was then heated to 310°C for 40 minutes at a heating rate of 200°C/hr. The resulting gravel was ground to a dark green powder and added, with stirring, to 800 mL of distilled water. The stirring was continued for 30 minutes. Any non-dispersible solids (<5%) were removed by centrifuging at 4000 rpm for 10 minutes to leave an olive green transparent sol. The sol consisted of single phase fluorite nanocrystals with 10 to 15 nm particle size and a primary crystallite size of 5 nm (see Figure 3(a)). This sol was then used to impregnate a suitable high surface area and porous support (γ-Al_2O_3), dried and fired to 600°C

for 30 minutes. The catalyst was then activated by reduction at 850°C for 2 hours in 5% H_2/N_2, to produce a fine dispersion of copper metal on the surface of $Ce_{0.75}La_{0.15}O_{2-x/2}$ nanocrystals which in turn were dispersed on γ-Al_2O_3. On exposure to air, the metal dispersion partially reoxidised to give a fine dispersion of Cu_2O on nanocrystals of $Ce_{0.75}La_{0.15}O_{2-x/2}$, as can be seen in Figure 3(b) for the undispersed material.

Example 3

Rhodium Metal Catalyst on Yttria Stabilised Zirconia Nanocrystals

(i) Zirconia Hydrate Gel

Small quantities of zirconium basic carbonate (total quantity 60 g) were added to 6M HNO_3 (43 mL). A further portion of zirconium basic carbonate (40 g) was then slurried with water before adding to the acid mixture. The mixture was heated with stirring and after 10 to 15 minutes a clear sol developed. After diluting with distilled water (500 mL) and stirring for 20 minutes, the mixture was allowed to cool to room temperature. 880 ammonia (23 mL) was then added to water (880 mL) with stirring. The zirconium sol was added slowly to this mixture over 10 minutes with stirring. The resultant was allowed to settle and the supernatant decanted off. The sol was washed 4 times with 2 L of distilled water. The resultant gel was decanted to 900 mL, and 100 mL of HNO_3 was added. The mixture was centrifuged and the supernatant discarded to leave acid conditioned $ZrO(OH)_2.xH_2O$ hydrate gel.

(ii) Rhodium Metal Catalyst on Yttria Stabilised Zirconia Nanocrystals

Yttrium nitrate pentahydrate (8.16 g) and $Rh(NO_3)_3.xH_2O$ solution (13.21% Rh; 2.07 g) were added to 15 mL of distilled water and dissolved to give an orange/red clear solution. This was added with mixing to a wet

zirconia hydrate gel (125 g; containing 10.5 g ZrO_2; from step (i) above) and homogenized in a high shear mixer for 2 to 3 minutes. The resulting slurry was dried to a soft crumbly gel at 40°C (about 70% water by weight) and placed in a sealed reactor vessel. The vessel was heated to 295 to 300°C for 15 minutes and pressure was released after this time from 1020 psi to 600 psi (72 to 43 bar) quickly to remove excess nitric acid. The rector vessel was then cooled to room temperature quickly and the product added to 900 mL of distilled water and stirred for 1 hour to give a brown/beige translucent sol. Any non-dispersible product was again centrifuged off at 4000 rpm for 10 minutes. The resultant sol was transparent and beige in colour, and consisted of single phase cubic stabilised zirconia nanocrystals containing rhodium within the lattice (see Figure 4(a)). The average particle size of the sol was about 20 nm with a primary crystallite size of about 8 to 9 nm. This sol was used to impregnate a suitable support (γ-Al_2O_3), and dried and fired to 600°C for 30 minutes. The powder was then reduced at 900°C for 3 hours in 5% H_2/N_2 to produce highly dispersed rhodium metal entirely on the surface of yttria stabilized zirconia nanocrystals in turn dispersed on gamma alumina. The x-ray diffraction pattern of the undispersed material is shown in Figure 4(b).

Claims

1. A process for the production of a product comprising nanocrystalline particles, which particles comprise at least one metal, or at least one metal oxide, substantially dispersed on the surface of at least one metal oxide, or mixed metal oxide, which process includes the steps of:

(a) heating a mixture including at least one wet hydrous metal oxide, or wet hydrous mixed metal oxide, and at least one reducible metal salt, to form a wet gel;

(b) heating the wet gel to the decomposition temperature of the reducible metal salt; and

(c) reducing the resultant composition.

2. A process as claimed in Claim 1, wherein any non-dispersible product formed during steps (a) and/or (b) is removed by dispersing the product of step (b) into an aqueous solvent to form a sol, followed by removal of any non-dispersible sediment.

3. A process as claimed in Claim 1 or Claim 2, wherein the mixture of wet hydrous metal oxide, or mixed metal oxide, and reducible metal salt is heated at between room temperature and 120°C, and/or for between 1 and 24 hours.

4. A process as claimed in any one of the preceding claims, wherein the reducible metal salt is a metal nitrate, a metal chloride, a metal perchlorate, a metal acetate, a metal carbonate or a higher metal oxide.

5. A process as claimed in Claim 4, wherein the salt is a metal nitrate or a metal chloride.

6. A process as claimed in any one of the preceding claims, wherein the product of step (a) is heated in a controlled pressure/water atmosphere.

7. A process as claimed in Claim 6, wherein the product of step (a) is heated to between 220 and 330°C, and/or at a heating rate of between 10 and 500°C per hour, and/or for between 1 and 60 minutes.

8. A process as claimed in any one of Claims 1 to 5, wherein the product of step (a) is heated in a furnace or in an open atmosphere.

9. A process as claimed in Claim 8, wherein the product of step (a) is heated at a heating rate of between 10 and 500°C per hour, and/or for between 1 and 180 minutes.

10. A process as claimed in any one of the preceding claims, wherein the reduction is performed in 5% H_2/N_2, and/or at atmospheric pressure, and/or at 800°C to 1000°C.

11. A nanocrystalline product obtainable by a process as defined in any one of the preceding claims.

12. A process for the preparation of a coated or impregnated substrate, which comprises coating or impregnating a substrate with a product according to Claim 11.

13. A process for the preparation of a coated or impregnated substrate, which comprises a process as claimed in any one of Claims 1 to 10, but with the additional step that the product of step (b) is dispersed onto a

substrate before or after carrying out step (c).

14. A process as claimed in Claim 12 or Claim 13, wherein the substrate is γ-Al_2O_3.

15. A product obtainable by a process as defined in any one of Claims 12 to 14.

16. A product as claimed in Claim 15, which is a catalyst.

17. A catalyst comprising a product as claimed in Claim 11, coated or impregnated on a catalyst support.

18. A catalyst comprising nanocrystalline particles, which particles comprise at least one active metal, or at least one active metal oxide, substantially dispersed on the surface of at least one supporting metal oxide, or supporting mixed metal oxide, and a catalyst support, wherein no more than 1% of active metal/metal oxide is presented/dispersed on the catalyst support.

19. The use of a product according to Claim 11 in the manufacture of a catalyst.

Fig 1.

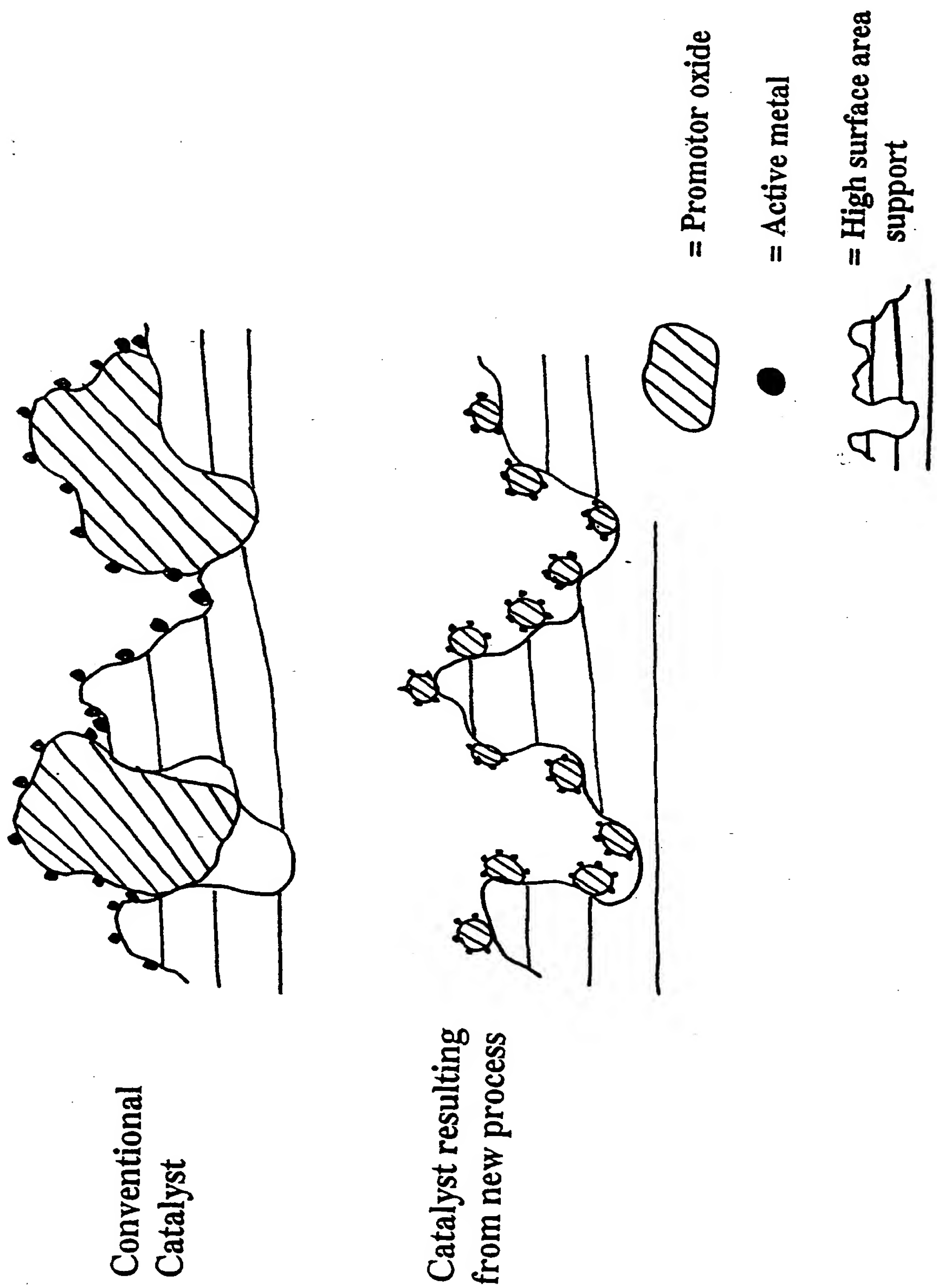

Conventional Catalyst
Catalyst resulting from new process
= Promotor oxide
= Active metal
= High surface area support

Fig 2.

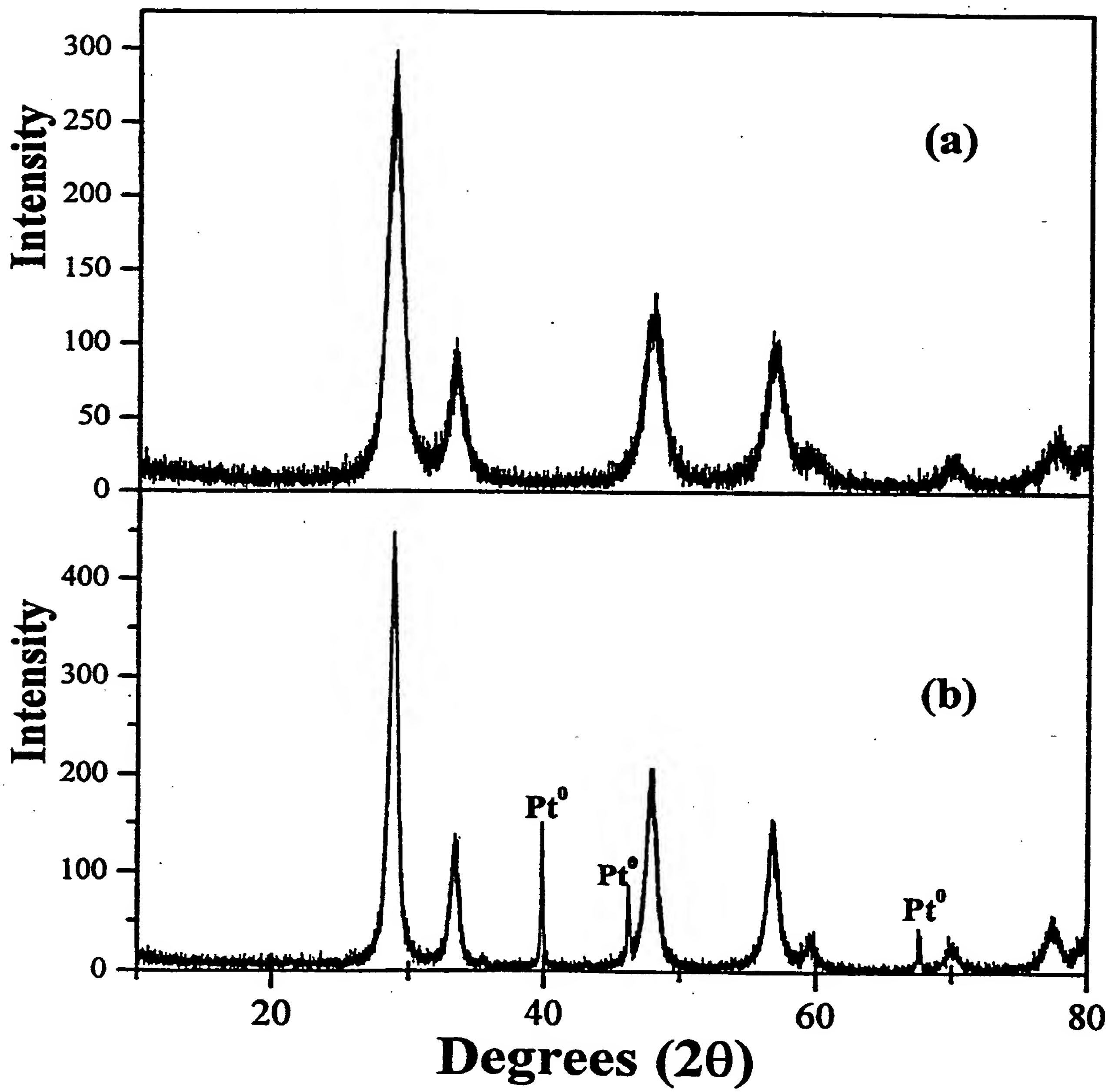

300
250
200
150
100
50
0
Intensity
(a)
400
300
200
100
0
Intensity
(b)
Pt⁰
Pt⁰
Pt⁰
20
40
60
80
Degrees (2θ)

Fig 3.

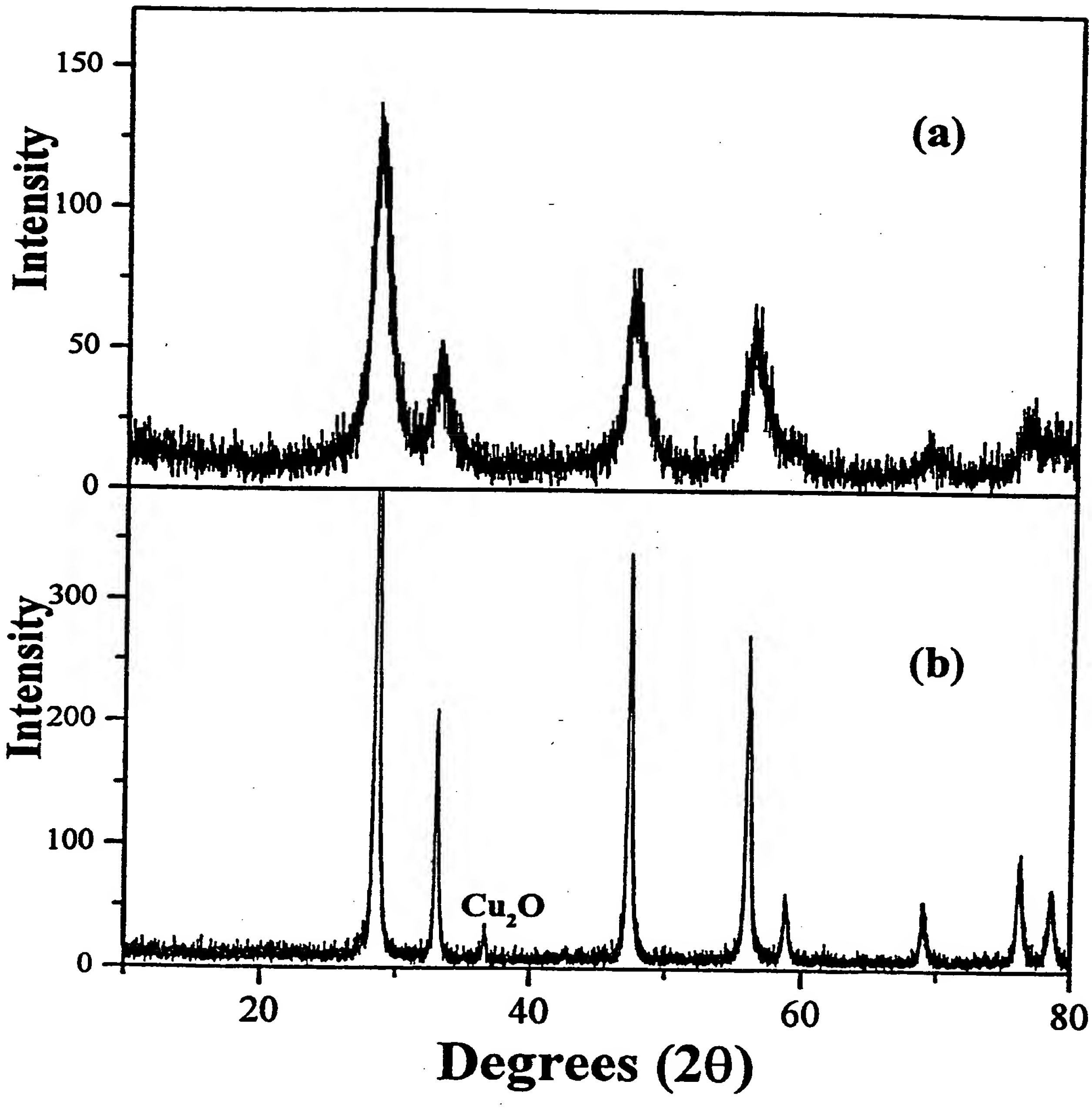
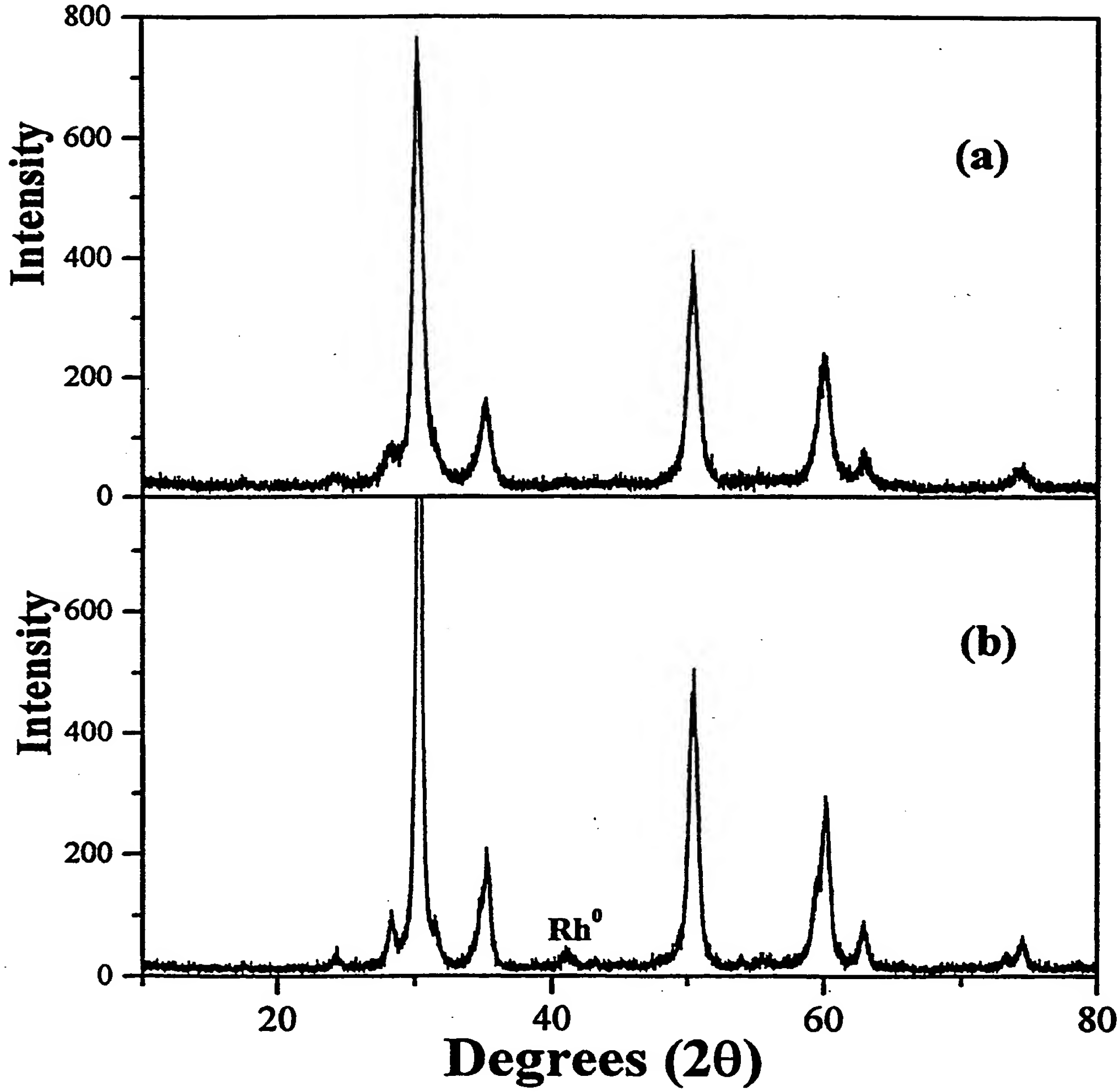

(a)
Intensity
150
100
50
0
(b)
Intensity
300
200
100
0
Cu$_2$O
20
40
60
80
Degrees (2θ)

Fig 4.


800
600
400
200
0
Intensity
(a)
600
400
200
0
Intensity
(b)
Rh^0
20
40
60
80
Degrees (2θ)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/03657

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J37/00 B01D53/94 C01F17/00 C01G25/00 B01J35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J B01D C01G C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 522 191 A (ATOMIC ENERGY AUTHORITY UK) 23 August 1978 (1978-08-23) the whole document ---	1,3-6, 8-19
A	EP 0 078 098 A (ATOMIC ENERGY AUTHORITY UK) 4 May 1983 (1983-05-04) the whole document ---	1,2,4,5, 8,9,11, 17
P,A	WO 98 51617 A (UNIV WARWICK ;BHATTACHARYA ASHOK KUMAR (GB); HARTRIDGE ADRIAN (GB)) 19 November 1998 (1998-11-19) cited in the application page 4, line 20 - line 29 -----	1-19

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 January 2000	09/02/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
PCT/GB 99/03657

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 1522191	A	23-08-1978	NONE		
EP 0078098	A	04-05-1983	CA 1186195	A	30-04-1985
			GB 2102780	A,B	09-02-1983
			JP 1626853	C	28-11-1991
			JP 2049249	B	29-10-1990
			JP 58055334	A	01-04-1983
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WO 9851617	A	19-11-1998	NONE		